IJ-82-3

REQ. NO. 2-9103

CONTRACT REPORT NO. OSQ82-00021

CHARACTERIZATION AND TESTING OF SYNCRUDE, CANSTAR, AND IRISH COVE LIMESTONES FOR USE IN SUMMERSIDE FBC

Prepared for

ENERGY, MINES AND RESOURCES CANADA

22 July 1982

Prepared by

Irving Johnson
276 Woodstock Avenue
Clarendon Hills, Ill. 60514
(312) 323-7540

Contract No. OSQ82-00021

18pp

CHARACTERIZATION AND TESTING OF SYNCRUDE, CANSTAR, AND IRISH COVE LIMESTONES FOR USE IN SUMMERSIDE FBC

SUMMARY

Three limestones, Syncrude (SY-1), Canstar (CS-1), and Irish Cove (NS-1) have been tested for use for the control of SO2 emission from fluidized bed combustors.

All three limestones have acceptable shock calcination characteristics, i.e., the amount of fine material generated when these limestones are injected into a hot FBC is expested to be small enough so as to not pose a practical problem.

The extent of sulfation of these three limestones was slightly lower than the average limestone used for the control of SO2 emission from FBC's. There is not a significant difference between these three stones as seen by the following comparison:

	Syncrude (SY-1)	Canstar (CS-1)	Irish Cove (NS-1)
Retention Ca/S = 3	47%	52%	51%
Feed Rate* for 80% Retention *kg/kg coal	1.14	1.07	1.07

The Irish Cove (NS-1) limestone is compared with another sample of Irish Cove limestone (NS-9) and Calpo limestone (NS-10) for use in the Nova Scotia Power Corporation Test Rig. Irish Cove (NS-1) is significantly poorer than the other two stones for this application.

Detailed descriptions of the test results and predictions follow.

EXPERIMENTAL STUDY OF LIMESTONE SYNCRUDE (SY-1)

Preparation for Testing- The stone was received as a -18+20 mesh washed sample. Examination showed no significant breakup on shipping and the sample was used without further treatment. A sample was analyzed for calcium; found 92.0% (as CaCO3). This result is in fair agreement with the value of 90.7% reported by CANMET for this stone. The bulk density of this stone was measured by slowly pouring the granular material into a measured volume. A value of 1.5 g/cc was found. The apparant density of the stone was measured by water displacement. A value of 2.75 g/cc was found. These values can be used to compute the voidage of the material in loose packing; a value of 0.45 was found. This voidage is approximately what would be found for a bed of this stone at minimum fluidization.

Shock Calcination- A six gram sample was prepared by exhaustively sieving on the 20-mesh sieve. This sample was shock heated by being placed in a preheated furnace. After 20-min heating the sample was removed and cooled. The fraction that passed through a 20-mesh sieve was determined; about 0.4 w/o passed through the sieve. There is no evidence from this test that this stone will undergo extensive decrepitation when injected into a hot fluidized bed combustor.

Extent of Sulfation- A sample of about 0.5 g was first calcined and then sulfated in the sulfation apparatus. Completeness of calcination was determined by heating until a constant weight was obtained. The weight loss on complete calcination was 42.1% which may be compared to a value of 41.0% computed from the CaCO3 and MgCO3 content of the stone. The small difference reflects the water present in the stone with the clay minerals.

The extent of sulfation was determined by exposure of the calcined sample to a gas mixture containing 0.3 volume percent sulfur dioxide at 850 C and weighing periodically. From the weight gain, which was assumed to be due to the formation of CaSO4, the extent of sulfation was computed. The data are tabulated at the end of this section.

These sulfation data were used to determine the parameters a, k, n of the empirical equation:

$$x\ (\%) = a*(1-EXP(-k*t**n))$$

in which t is the time in minutes. A non-linear least squares method was used to obtain these parameters. The values of the parameters obtained are:

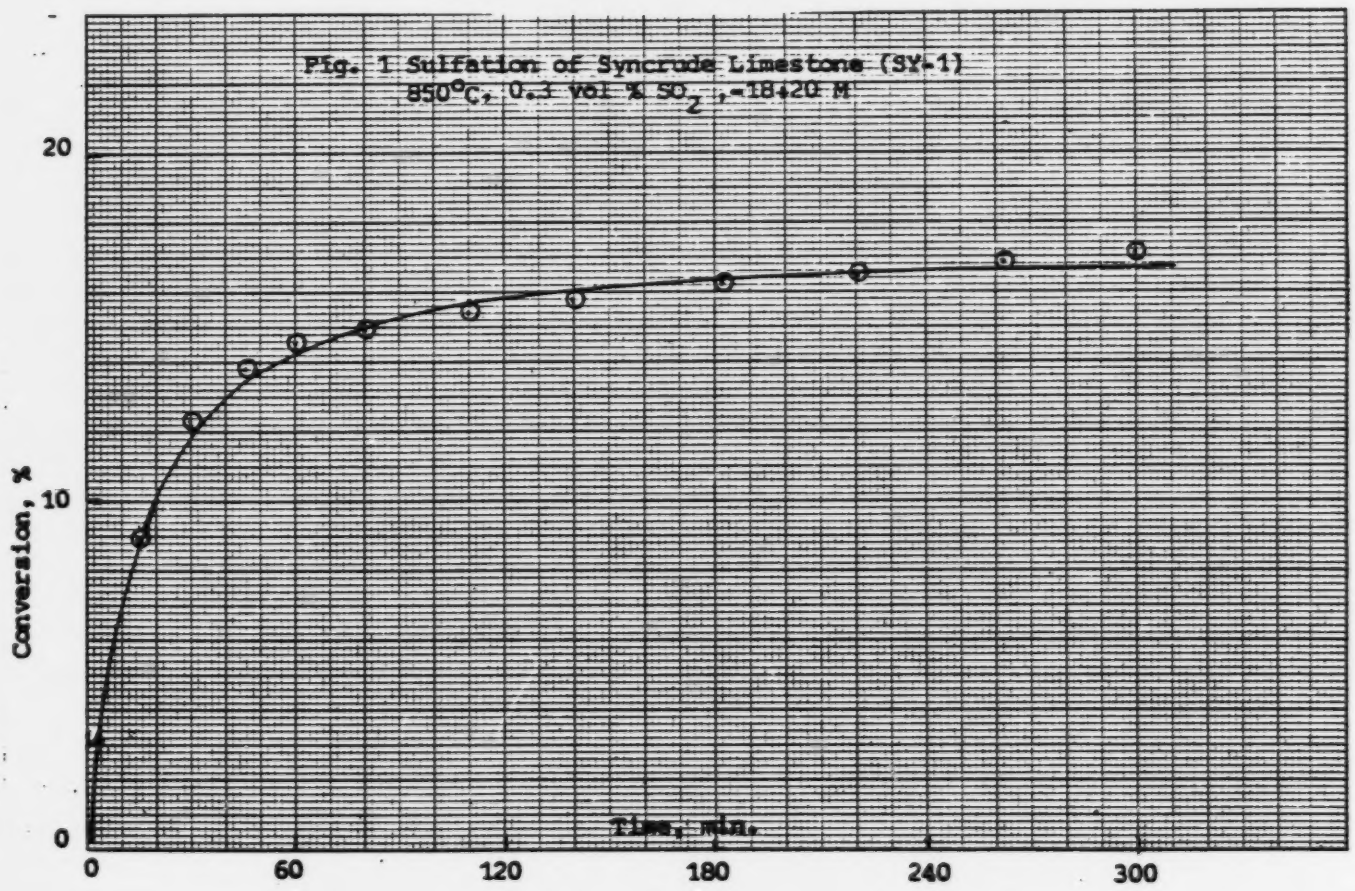
$$a = 16.77$$
$$k = 0.1467$$
$$n = 0.6293$$

The standard deviation of the difference between the observed and calculated values is 0.39%.

Sulfation of Syncrude Limestone (SY-1)

Time (min)	Conversion (%)
15	8.85
30	12.36
45	13.80
60	14.52
80	14.90
110	15.38
140	15.79
182	16.20
220	16.49
262	16.88
300	17.16

These data are compared to the computed curve on the figure that follows.



EXPERIMENTAL STUDY OF LIMESTONE CANSTAR (CS-1)

Preparation for Testing- The stone was received as a -18+20 mesh washed sample. Examination showed no significant breakup on shipping and the sample was used without further treatment. A sample was analyzed for calcium; found 90.2% (as CaCO3). This result is in good agreement with the value of 90.0% reported by CANMET for this stone. The bulk density of this stone was measured by slowly pouring the granular material into a measured volume. A value of 1.4 g/cc was found. The apparant density of the stone was measured by water displacement. A value of 2.6 g/cc was found. These values can be used to compute the voidage of the material in loose packing; a value of 0.47 was found. This voidage is approximately what would be found for a bed of this stone at minimum fluidization.

Shock Calcination- A six gram sample was prepared by exhaustively sieving on the 20-mesh sieve. This sample was shock heated by being placed in a preheated furnace. After 20-min heating the sample was removed and cooled. The fraction that passed through a 20-mesh sieve was determined; about 0.4 w/o passed through the sieve. There is no evidence from this test that this stone will undergo extensive decrepitation when injected into a hot fluidized bed combustor.

Extent of Sulfation- A sample of about 0.5 g was first calcined and then sulfated in the sulfation apparatus. Completeness of calcination was determined by heating until a constant weight was obtained. The weight loss on complete calcination was 40.6% which may be compared to a value of 41.1% computed from the CaCO3 and MgCO3 content of the stone. The small difference is probably within the uncertainty of the analyses.

The extent of sulfation was determined by exposure of the calcined sample to a gas mixture containing 0.3 volume percent sulfur dioxide at 850 C and weighing periodically. From the weight gain, which was assumed to be due to the formation of CaSO4, the extent of sulfation was computed. The data are tabulated at the end of this section.

These sulfation data were used to determine the parameters a, k, n of the empirical equation:

$$x\ (\%) = a*(1-EXP(-k*t**n))$$

in which t is the time in minutes. A non-linear least squares method was used to obtain these parameters. The values of the parameters obtained are:

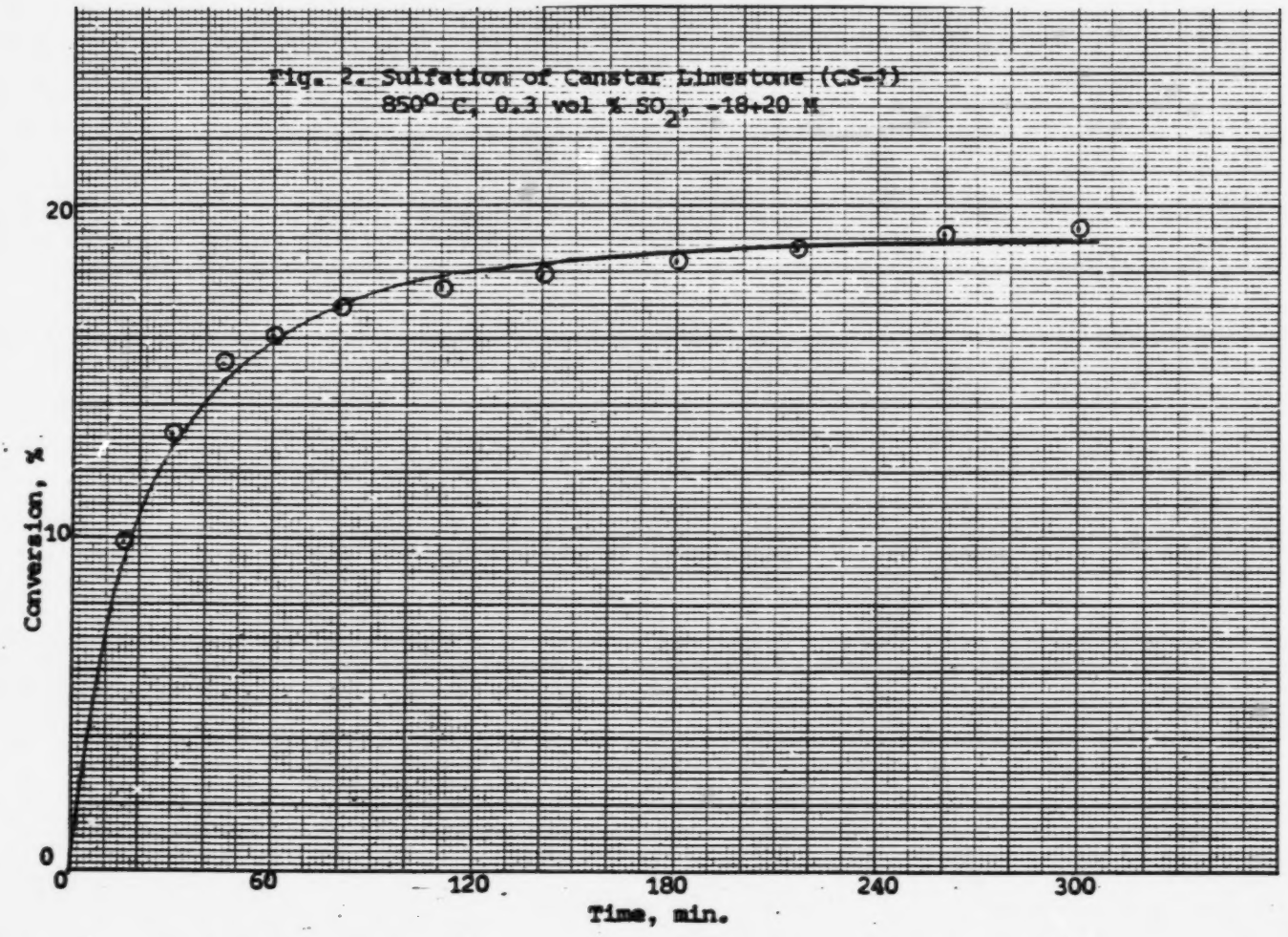
a = 18.90
k = 0.0956
n = 0.7264

The standard deviation of the difference between the observed and calculated values is 0.40%.

Sulfation of Canstar (CS-1) Limestone

Time (min)	Conversion (%)
15	8.91
30	13.09
45	15.25
60	16.08
80	16.90
110	17.46
140	17.87
180	18.33
216	18.74
260	19.07
300	19.34

These data are compared to the computed curve on the figure that follows.



EXPERIMENTAL STUDY OF LIMESTONE IRISH COVE (NS-1)

Preparation for Testing- The stone was received as a -18+20 mesh washed sample. Examination showed no significant breakup on shipping and the sample was used without further treatment. A sample was analyzed for calcium; found 95.6% (as CaCO3). This result is in poor agreement with the value of 93.2% reported by CANMET for this stone. The bulk density of this stone was measured by slowly pouring the granular material into a measured volume. A value of 1.4 g/cc was found. The apparant density of the stone was measured by water displacement. A value of 2.7 g/cc was found. These values can be used to compute the voidage of the material in loose packing; a value of 0.48 was found. This voidage is approximately what would be found for a bed of this stone at minimum fluidization.

Shock Calcination- A six gram sample was prepared by exhaustively sieving on the 20-mesh sieve. This sample was shock heated by being placed in a preheated furnace. After 20-min heating the sample was removed and cooled. The fraction that passed through a 20-mesh sieve was determined; about 0.4 w/o passed through the sieve. There is no evidence from this test that this stone will undergo extensive decrepitation when injected into a hot fluidized bed combustor.

Extent of Sulfation- A sample of about 0.5 g was first calcined and then sulfated in the sulfation apparatus. Completeness of calcination was determined by heating until a constant weight was obtained. The weight loss on complete calcination was 43.0% which may be compared to a value of 42.0% computed from the CaCO3 and MgCO3 content of the stone.The value for the calcium content found in this study was used. The small difference reflects the water present in the stone with the clay minerals.

The extent of sulfation was determined by exposure of the calcined sample to a gas mixture containing 0.3 volume percent sulfur dioxide at 850 C and weighing periodically. From the weight gain, which was assumed to be due to the formation of CaSO4, the extent of sulfation was computed. The data are tabulated at the end of this section.

These sulfation data were used to determine the parameters a, k, n of the empirical equation:

$$x\ (\%) = a*(1-EXP(-k*t**n))$$

in which t is the time in minutes. A non-linear least squares method was used to obtain these parameters. The values of the parameters obtained are:

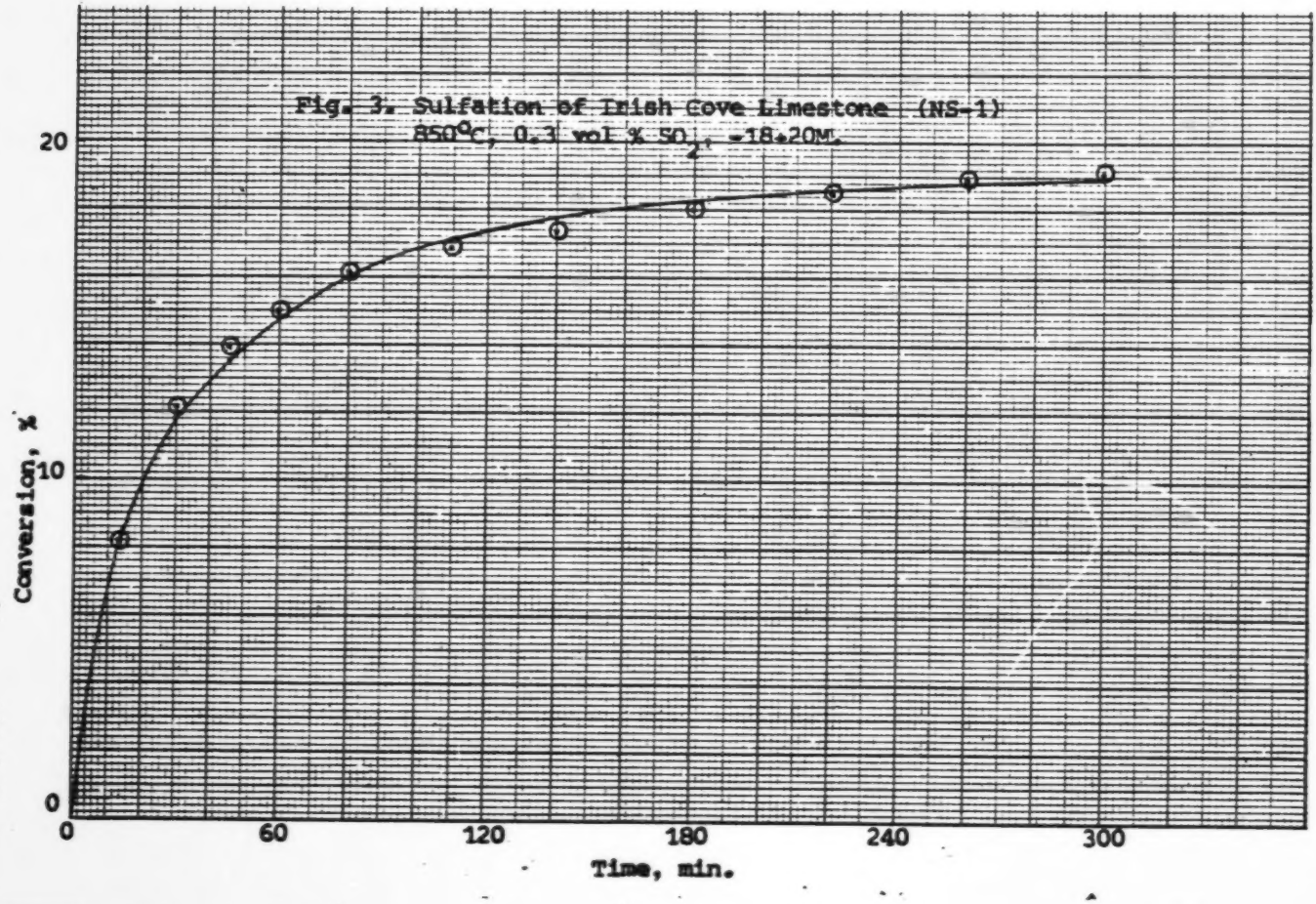
a = 19.00
k = 0.096
n = 0.6747

The standard deviation of the difference between the observed and calculated values is 0.33%.

Sulfation of Irish Cove (NS-1) Limestone

Time (min)	Conversion (%)
15	8.11
31	12.14
45	13.91
60	14.98
80	16.05
110	16.79
140	17.29
180	17.99
220	18.52
260	18.85
300	19.14

These data are compared to the computed curve on the figure that follows.



PREDICTION OF SULFUR DIOXIDE RETENTION IN FLUIDIZED BED COMBUSTORS

The sulfur dioxide retention as a function of the Ca/S molar feed ratio has been computed using the sulfation data obtained in this study and the Argonne model for sulfur capture in FBC's. The SO2 retention expected using the limestones studied has been estimated for the Summerside FBC.

FBC Operational Parameters- To use the Argonne model to predict SO2 retention requires that three parameters be estimated for the FBC. These parameters are: (1) the sulfur feed rate (moles/min), (2) the total quantity of calcium in the bed (moles), and (3) the effective gas flow rate (liters/min). The values of these parameters have been estimated for the Summerside FBC and the basis given in the previous report in this series (IJ-82-2).

The sulfur feed rate is only dependent on the coal feed rate and its sulfur content. A value of 57.29 moles/min is obtained for the sulfur feed rate, S , for the Summerside FBC.

The amount of calcium in the bed is dependent on the packing density of the stone, its calcium content as well as the bed dimensions and therefore is expected to vary slightly for different stones when used in the same combustor. For the three stones studied the following values of B have been obtained:

Limestone	Calcium in bed, B , (moles)
Syncrude (SY-1)	87700
Canstar (CS-1)	81000
Irish Cove (NS-1)	86400

The gas flow rate is dependent on the minimum fluidization gas velocity, which, in turn, is a function of the average particle density and size in the bed. This density is dependent on the individual stone because of differences in the apparent density and extent of sulfation. However, when the particle density of the three stones under consideration is computed the same value (2.2 g/cc) is obtained. Hence the same minimum fluidization velocity can be used for each stone. This leads to a value of 343,000 L/mim for the effective gas flow rate, G.

Predicted Sulfur Dioxide Retention- The sulfation data given in the experimental sections for each stone were use with the appropriate values of the FBC parameters to estimate the SO2 retention using the Argonne model as implemented in FORTRAN program SO2FBC. The results of the computations are given in Tables 1,2 and 3 and shown graphically on Fig. 4. The results obtained in a previous study of Havelock (NB-1) limestone for this same combustor is shown for comparison. These results can be used to compute the limestone feed rate (kg/kg coal) needed to achieve various values of the SO2 retention.

Quantity of Limestone Needed (kg/kg coal)

Retention,%	Syncrude	Canstar	Irish Cove	Havelock
60	0.69	0.63	0.61	0.42
65	0.78	0.70	0.68	0.47
70	0.87	0.79	0.78	0.51
75	0.99	0.91	0.90	0.57
80	1.14	1.07	1.07	0.65
85	1.38	1.31	1.35	0.76
90	-	-	-	1.01

It is seen that these three limestones are not as good as Havelock (NB-1) limestone for the control of SO2 emission from FBC's. The three limestones are not significantly different.

RUN SO2FBC Table 1 Predicted Retention for Syncrude Limestone in Summerside FBC

ENTER A,K & N FROM TGA EQN

16.77373,.14673,.62925

ENTER S,B,G FOR FBC CONDITIONS

57.29,87700.,343000.

CA/S	UTIL	RETENTION
0.50	16.77	8.38
1.00	16.71	16.71
1.50	16.55	24.83
2.00	16.33	32.66
2.50	16.04	40.11
3.00	15.71	47.12
3.50	15.32	53.63
4.00	14.89	59.55
4.50	14.41	64.83
5.00	13.89	69.43
5.50	13.34	73.35
6.00	12.77	76.64
6.50	12.21	79.36
7.00	11.66	81.61
7.50	11.13	83.46
8.00	10.63	85.00
8.50	10.15	86.28
9.00	9.71	87.36
9.50	9.29	88.28
10.00	8.91	89.07

STOP --

RUN SO2FBC Table 2. Predicted Retention For Canstar Limestone in Summerside FBC

ENTER A,K & N FROM TGA EQN

18.89933,.09557,.72644

ENTER S,B,G FOR FBC CONDITIONS

57.29,81000.,343000.

CA/S	UTIL	RETENTION
0.50	18.90	9.45
1.00	18.83	18.83
1.50	18.62	27.93
2.00	18.28	36.55
2.50	17.84	44.61
3.00	17.33	52.00
3.50	16.75	58.64
4.00	16.11	64.45
4.50	15.42	69.38
5.00	14.69	73.45
5.50	13.95	76.75
6.00	13.23	79.40
6.50	12.54	81.52
7.00	11.89	83.24
7.50	11.28	84.64
8.00	10.72	85.79
8.50	10.21	86.75
9.00	9.73	87.56
9.50	9.29	88.26
10.00	8.89	88.86

STOP --

RUN SO2FBC Table 3. Predicted Retention for Irish Cove Limestone in Summerside FBC

ENTER A,K & N FROM TGA EQN

19.00482,.09603,.67468

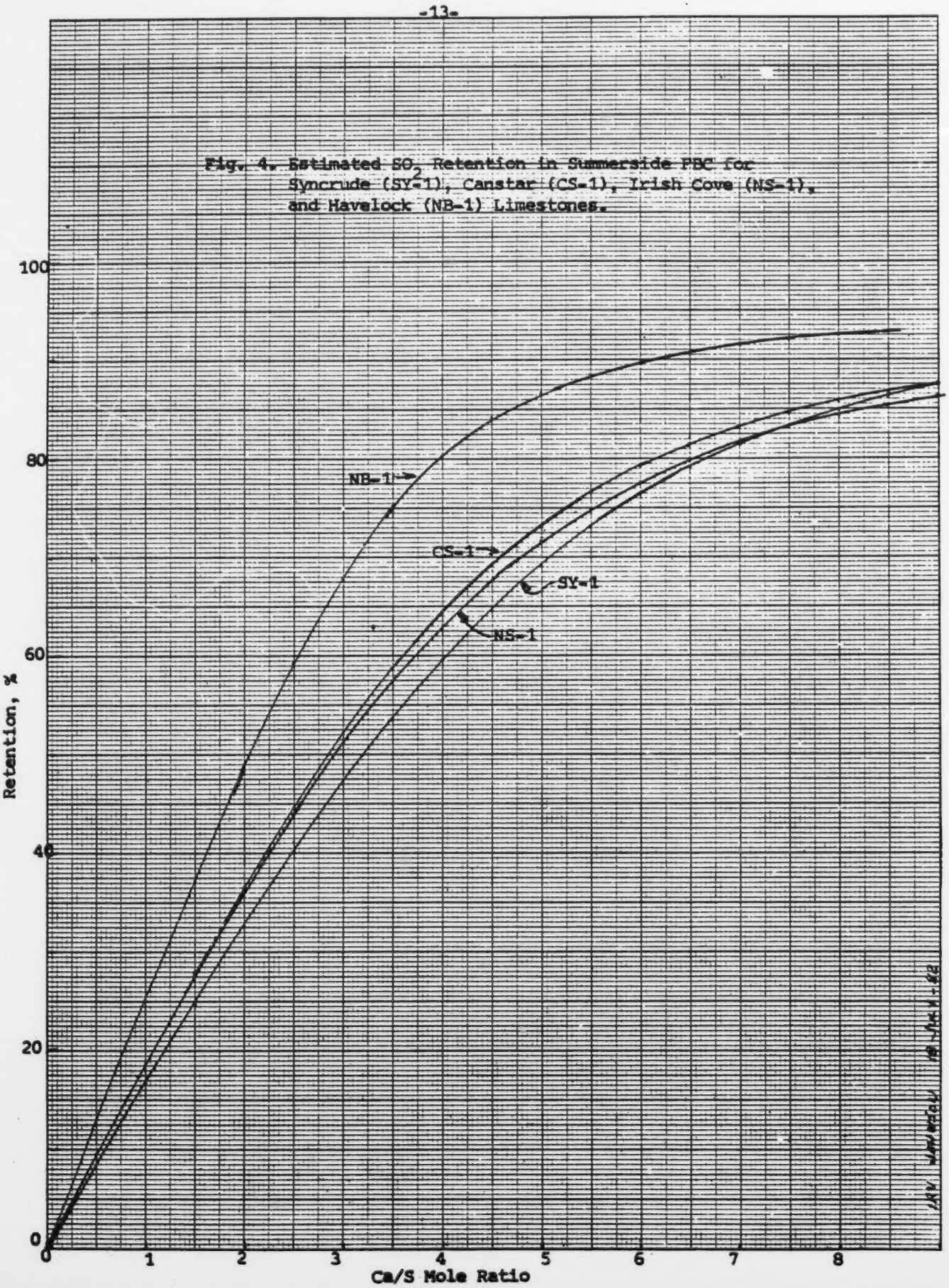
ENTER S,B,G FOR FBC CONDITIONS

57.29,86400.,343000.

CA/S	UTIL	RETENTION
0.50	18.99	9.50
1.00	18.84	18.84
1.50	18.52	27.78
2.00	18.10	36.19
2.50	17.60	44.00
3.00	17.04	51.13
3.50	16.43	57.50
4.00	15.76	63.05
4.50	15.06	67.78
5.00	14.34	71.72
5.50	13.63	74.97
6.00	12.94	77.63
6.50	12.28	79.81
7.00	11.66	81.61
7.50	11.08	83.10
8.00	10.54	84.35
8.50	10.05	85.40
9.00	9.59	86.31
9.50	9.17	87.09
10.00	8.78	87.76

STOP --

Fig. 4. Estimated SO_2 Retention in Summerside PBC for Syncrude (SY-1), Canstar (CS-1), Irish Cove (NS-1), and Havelock (NB-1) Limestones.



COMPARISON OF IRISH COVE WITH OTHER NOVA SCOTIA STONES

The SO2 retention for the sample of Irish Cove limestone (NS-1) has been compared to values obtained for other Nova Scotia stones when use in the Nova Scotia Power Corporation Test Rig using the Argonne model and the sulfation data obtained in this and previous studies. Fig. 5 compares Irish Cove (NS-1) with Irish Cove (NS-9) and Calpo (NS-10) limestones. It is seen that Irish Cove (NS-1) is not as good for SO2 emission control in the Test Rig as Irish Cove (NS-9). Both Irish Cove stones are less effective for this use than the Calpo limestone.

The quantities of limestone needed (kg/kg coal) are compared below. Recall that the Test Rig is to use 2% S coal in the tests.

Quantity of Limestone Needed (kg/kg coal)

Retention	Irish Cove(NS-1)	Irish Cove(NS-9)	Calpo(NS-10)
60	0.28	0.21	0.11
65	0.33	0.24	0.12
70	0.39	0.28	0.14
75	0.49	0.32	0.16
80	0.60	0.40	0.20
85	-	0.51	0.29
90			~0.65

Table 4. Predicted Retention for Irish Cove Limestone in Nova Scotia Power Co. Test Rig

ENTER A,K & N FROM TGA EQN

19.00482,.09603,.67468

ENTER S,B,G FOR FBC CONDITIONS

2.448,6147.,44500.

CA/S	UTIL	RETENTION
0.50	18.90	9.45
1.00	18.45	18.45
1.50	17.87	26.80
2.00	17.23	34.46
2.50	16.56	41.39
3.00	15.86	47.58
3.50	15.14	53.00
4.00	14.42	57.70
4.50	13.72	61.72
5.00	13.03	65.14
5.50	12.37	68.05
6.00	11.75	70.52
6.50	11.17	72.62
7.00	10.63	74.43
7.50	10.13	75.99
8.00	9.67	77.34
8.50	9.24	78.53
9.00	8.84	79.57
9.50	8.47	80.50
10.00	8.13	81.32

STOP --

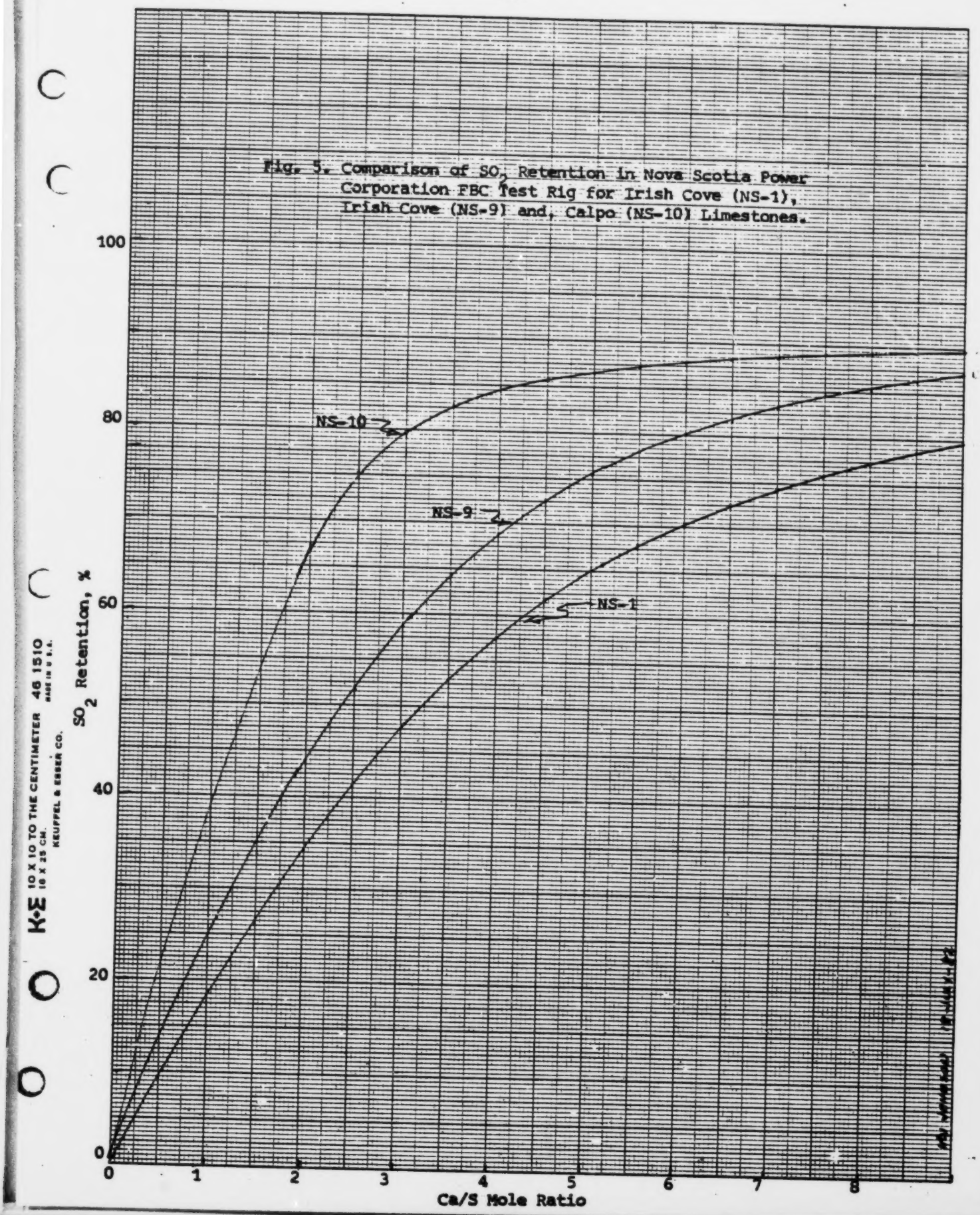


Fig. 5. Comparison of SO_2 Retention in Nova Scotia Power Corporation FBC Test Rig for Irish Cove (NS-1), Irish Cove (NS-9) and, Calpo (NS-10) Limestones.